

STUDIES OF THE AGGLOMERATION AND REACTIONS OF CA AND K DURING PYROLYSIS AND GASIFICATION

*Naresh Shah¹, Frank E. Huggins¹, Anup Shah¹, Gerald P. Huffman¹,
Robert G. Jenkins², and Andrzej Piotrowski³*

¹University of Kentucky, Lexington, KY 40506

²University of Cincinnati, Cincinnati, OH 45221

³Penn State University, State College, PA 16802

INTRODUCTION

Efficient catalytic processes are the key to successful and economical coal gasification. With suitable catalysts, gasification rates can be significantly enhanced or the process can be operated at substantially lower temperatures. The importance of alkalis and alkaline earths as catalysts for gasification process is well known (1,2). For over a century alkali additives such as caustic soda and/or lime have been used to promote the reactions of steam and air with coal and charcoal (3). Ca and Na occur naturally in macerals of lignites in a highly dispersed form that is as close to an ideal catalyst dispersion as possible (4,5). Catalytic effects of alkalis on the gasification rates for coal (6,7), char (8,9), graphite (10,11) and wood (12) have been investigated. Enhanced gasification rates of >10 times has been observed with Ca rich lignites compared with base lignite from which Ca has been removed (13). However, the exact role played by these catalysts is not yet clearly understood. Hence there is considerable interest in the structural forms of these catalysts in their dispersed state, after pyrolysis, during gasification and after reaction. Determination of catalyst structures at these various stages has proven difficult because of the high dispersion (often molecular) and relatively very low catalyst concentrations ($\approx 1-2\%$).

XAFS (X-Ray Absorption Fine Structure) spectroscopy is a powerful structural analysis technique that has unique ability to focus on only one element and provide information about its bonding and the short range structure. It is capable of providing excellent signal to noise ratio at dilute concentrations and at elevated temperatures. It is ideally suited for coal as it can give information on the element of interest at concentrations as low as 100 ppm without elaborate sample preparation (14). In theory, XAFS analysis can be carried out for any element of interest. However, due to X-ray attenuation problems, XAFS has been successful only for elements above S in the periodic table without good vacuum conditions. Thus, even though Na is an important element in coal gasification, it has not been directly analyzed. Ca and K are the two most important elements of interest in coal that have been studied using XAFS analysis.

CCSEM (Computer Controlled Scanning Electron Microscopy) can be used to monitor the physical dispersion of the catalysts in the samples which have undergone advanced stages of pyrolysis and gasification. CCSEM can measure the sizes and compositions of about 500 particles per hour enabling quantitative measurements of size distributions and weight distributions of inorganic phases in coal and chars (15).

EXPERIMENTAL

XAFS spectroscopy was performed at SSRL during dedicated running conditions. A pure He path to the sample was employed to minimize attenuation of X-rays. Spectra were recorded from ≈ 100 eV below to ≈ 500 eV above the K edges of Ca and K in coal using a double crystal Si (111) monochromator. The fluorescent X-rays were measured by a Stern-Heald type detector (16). The in-situ experiments were carried out in a specially designed furnace (17). Data was collected on a PDP 11/23 computer and analyzed on a MicroVax II at the University of Kentucky. Calcite and KCl were used as primary standards for calibration purposes for Ca and K respectively.

Ca loaded chars were prepared and measured for reactivity by Radovic et al. from a Ca rich lignite (Falkirk, ND) and from ion-exchangeable phenol formaldehyde polymer (18). Chars were prepared by slow (up to 1 hr) and rapid (entrained flow reactor, residence time ≈ 0.3 sec) pyrolysis at 800 and 1000°C in N_2 atmosphere.

RESULTS

As reported earlier, XAFS on lignites without any heat exposure showed that Ca is bonded to carboxyl groups and is molecularly dispersed throughout the lignite macerals (4,5). Fourier transformation of EXAFS provides a radial structure function (RSF) which is closely related to the radial distribution of the shells of neighboring atoms of the central absorbing atom (19,20). Fig. 1 shows several such RSFs. In CaO the nearest neighbor shell of central Ca atom is made up of oxygen atoms at 2.4 Å and then there are shells of Ca, O, Ca, Ca and Ca at about 3.4, 4.0, 4.8, 5.9 and 6.8 Å respectively. These values agree very well with values determined based on NaCl-type structure.

In the Ca-loaded lignite RSF, however, there is only one major peak at approximately 2.4 Å due to the nearest oxygen shell. This is due to non-crystallinity and highly dispersed state of Ca atoms in the lignite macerals. After rapid pyrolysis of this lignite, the RSF does not change significantly. At the temperature conditions used in rapid pyrolysis treatment, the carboxyl groups should be driven off. However, even under such conditions, the nearest neighbor oxygen shell surrounding Ca is virtually unchanged. Moreover, lack of any detectable neighbor shells at longer distances indicate that Ca must still be in a highly dispersed state in the devolatilized, non crystalline char matrix. As the severity of pyrolysis increased (either increasing time or temperature or both), two processes take place: [1] Carboxyl groups start breaking up as the char devolatilizes. In the nearest neighbor shell of Ca, number of O atoms decreases (21). The second shell distance also moves towards that of the Ca-Ca distance in Ca-O and away from the Ca-C distance in the carboxyl groups (22). [2] Ca atoms become more mobile and start agglomeration. This clustering results in longer range order. Thus, as shown in Fig. 1, with slow pyrolysis treatment, the RSF looks increasingly like the CaO RSF as the intensity due to shells of atoms further away increases. Even after slow pyrolysis treatment, there is some Ca left in the dispersed state in the matrix. This is evident in Fig. 1D as a major peak of the nearest O shell like that in the untreated coal. Since Ca atoms are no much less dispersed, the effective surface area of the catalytic sites is reduced dramatically. This directly influences the reactivity in the gasification process.

To study the onset of this transformation, in-situ experiments were designed (23). Samples of coal and char loaded with Ca were heated while XAFS spectra were measured. To simulate pyrolysis, initially only He was flowing through the in-situ

furnace. After heating to about 500°C, 90% He - 10% O₂ was introduced to simulate gasification. Unfortunately, due to furnace heater capacity limitations, the samples could be heated only up to 500°C and the experiment could not be carried out to attain the state of slow pyrolysis as mentioned above. Due to this limitation only conditions of very mild pyrolysis were simulated and as expected no major changes in RSF were detected in this type of experiments.

Fig. 2 shows a series of XANES spectra as a function of heating conditions. As the temperature is increased, there is some broadening and loss of resolution of the XANES features. There are no significant peak shifts, peak removal or new peak appearance. Introduction of oxygen into the in-situ cell, to simulate gasification, accelerated these changes only very slightly. A small pre-edge peak intensifies and grows with heat treatment. This peak, presumably, represents a transition of the photoelectron from 1s to a hybridized 3d/2p level formed by Ca to O bonding. The intensity of this peak may, therefore, be indicative of the degree of loss of carboxyl molecules and Ca-O clustering to reach the final stage of CaO. An edge fitting computer program was used to generate the XANES by using the sum of a step and several Lorentzian functions (24). Thus each feature of XANES can be isolated and studied separately. Fig.3 shows the area of this pre-edge peak as a function of heating conditions. The pre-edge feature intensity may vary with the symmetry of the site (25) and it is possible that the Ca site becomes more asymmetric with pyrolysis.

Fig.4 shows a series of XANES spectra of K loaded char at differing heating conditions. Unlike Ca, the XANES spectra of K loaded char indicate a distinct transformation leading to a possibility of phase change. On switching from pyrolysis to gasification conditions, K dispersed in the coal char rapidly agglomerates and forms K₂CO₃ which does not undergo any further transformation under the mild gasification conditions of our experiments.

CCSEM analysis is not well suited for the early stages of pyrolysis and gasification as the catalytic species are very fine and uniformly dispersed. However, in advanced stages of gasification, when the agglomeration of catalysts occurs, CCSEM methods can be used. Presently, we are working with the severely pyrolyzed and ash samples. X-ray mapping feature of CCSEM is very promising. In this way we can directly observe the discrete inorganic particles and the dispersed catalysts in organic phase (26). With pyrolysis and gasification, we can study the agglomeration and reactions of both these phases. Ternary phase diagrams give further insight in this type of reactions (27).

CONCLUSIONS

XAFS spectroscopy is an excellent method to investigate structure of Ca and K catalysts. Ca agglomerates during pyrolysis and gasification at high temperatures. It forms CaO particles under slow pyrolysis conditions. In-situ methods can be used to study this in further detail. Carboxyl-bound K in lignites forms K₂CO₃ during gasification but does not exhibit any major changes under mild pyrolysis and gasification conditions. CCSEM is an excellent tool for analyzing agglomeration and clustering at advanced stages of gasification. X-ray mapping provides direct evidence of presence of bulk discrete mineral phases and dispersed catalytic species in the matrix. Agglomeration and reaction of these phases can be directly observed with this tool.

ACKNOWLEDGEMENTS

This work was supported by the Gas Research Institute. We also acknowledge the U.S. DOE for its support of the Stanford Synchrotron Radiation Laboratory, where the XAFS experiments were performed.

REFERENCES

1. Fuel, special issue on fundamentals of catalytic coal and carbon gasification 62(2), 1983
2. Fuel, special issue on conf. on C and catalysis, 63(8), 1984
3. T. duMotal, British patent 2548 (1887)
4. F.E. Huggins, G.P. Huffman, F.W. Lyttle, R.B. Greegor, Proc. of 1983 Int. COnf. on coal Sc., Pittsburgh, (1983) p.679-682
5. G.P. Huffman, F.E. Huggins, The chemistry of low rank coals, Ed. H.H. Schobert, ACS, (1984) p.159-174
6. W.P. Haynes, S.J. Gasior, A.J. Forney, ACS, Advances in Chemistry Series, 131, (1974), p.179
7. J.E. Gallagher, C.A. Euker, Energy Research, (1980), p.4
8. N. Kayembe, A.H. Pulsifer, Fuel, 55, (1976), p.211
9. D.W. McKee, C.L. Spiro, P.G. Kosky, E.J. Lamby, ACS Fuel Div. preprints, 27(1), (1982), p.74
10. K. Otto, L. Bartosiewicz, M. Shelef, Carbon, 17, (1979), p.351
11. D. W. McKee, Carbon, 17, (1979), p.419
12. R. A. Ross, P. Fong, Ind. Eng. Chem. Prod. Res. Dev., 21, (1981), p.197
13. E. J. Hippo, R.G. Jenkins, P.L. Walker, Fuel, 58, (1979), p.338
14. J. Wong, C.L. Spiro, D.H. Maylotte, F.W. Lyttle, R.B. Greegor, EXAFS and Near Edge Structure III, Springer Verlag, (1984), 362-367
15. F.E. Huggins, G.P. Huffman, R.J. Lee, ACS Symp. Ser. 205, 'Coal and Coal Products: Analytical characterization techniques' (Ed: E.L. Fuller), (1982), p.239-258.
16. E.A. Stern, S. Heald, Rev. Sci. Instrum., 50, (1979), 1579.
17. Available from the EXAFS Co., Seattle, WA
18. L.R. Radovic, P.L. Walker, R.G. Jenkins, Fuel, 62, (1983), p.209
19. P.A. Lee, P.H. Citrin, P. Eisenberger, B.M. Kincaid, Rev. Mod. Phys., 53, (1981), 769
20. G. S. Brown, S. Doniach, 'Synchrotron Radiation Research, Eds.: H. Winick, S. Doniach, Plenum PRes, (1980), 353-385
21. F.E. Huggins, N. Shah, G.P. Huffman, F.W. Lyttle, R.B. Greegor, Fuel, To be published.
22. F.E. Huggins, G.P. Huffman, N.Shah, R.G. Jenkins, F.W. Lyttle, R.B. Greegor, Fuel, 67, (1988), 938.
23. F.E. Huggins, G.P. Huffman, N. Shah, F.W. Lyttle, R.B. Greegor, R.G. Jenkins, Physica B, to be published.
24. R.B. Greegor, Edgefit computer program.
25. G.A. Waychunas, G. E. Brown Jr., C.W. Ponader, W.E. Jackson, Nature, 332(17), (1988), 251
26. G.P. Huffman, F.E. Huggins, R.W. Shoenberger, J.S. Walker, F.W. Lyttle, R.B. Greegor, Fuel, 65, (1986), p.621-632.
27. G.P. Huffman, F.E. Huggins, N. Shah, these preprints.

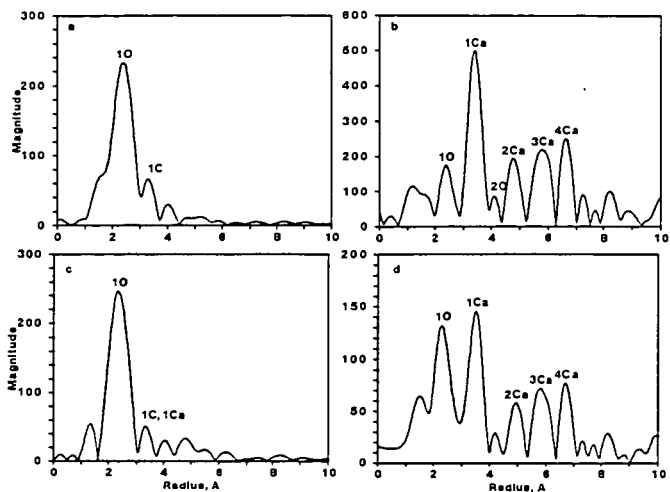


Fig. 1 Radial Structure Function of Ca K-edge EXAFS. (A) Ca loaded Falkirk lignite; (B) CaO; (C) Lignite char after Rapid pyrolysis at 1000°C; (D) Lignite char after slow pyrolysis at 1000°C.

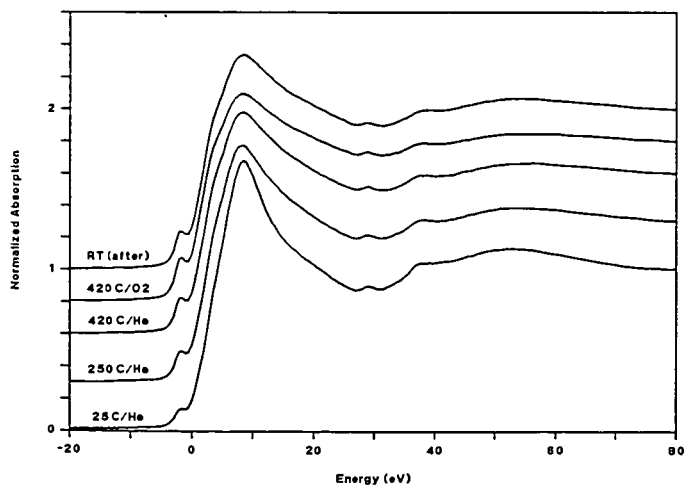


Fig. 2 In-situ XANES spectra of Ca-loaded lignite under He and then 10%O₂-90%He atmosphere at varying pyrolysis/gasification conditions.

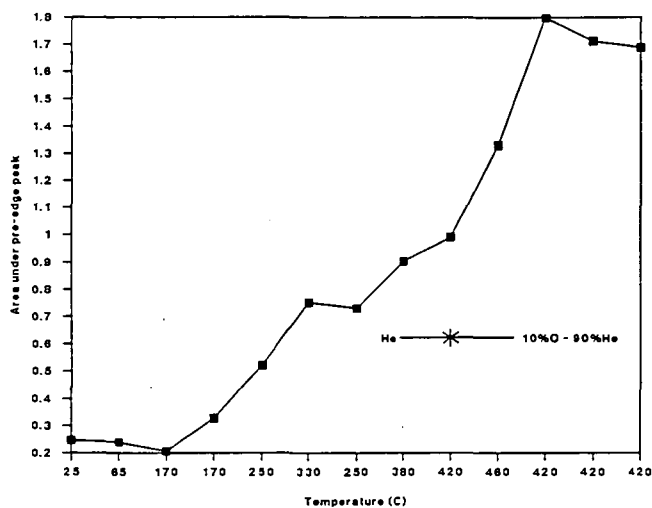


Fig. 3 Area under pre-edge peak of XANES spectra of Ca-loaded lignite at varying pyrolysis/gasification conditions.

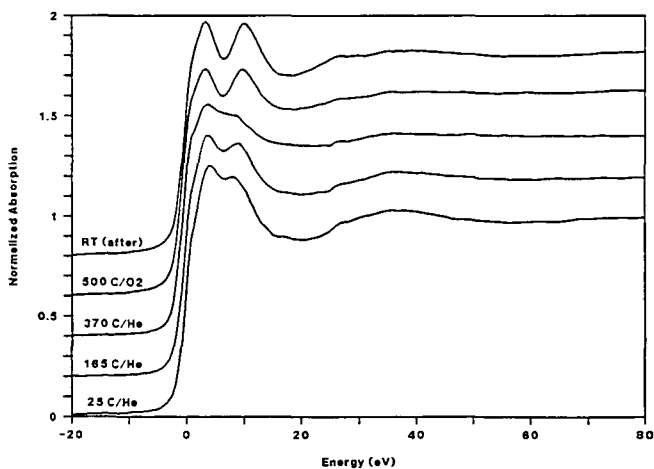


Fig. 4 In-situ XANES spectra of K-loaded lignite under He and then 10%O₂-90%He atmosphere at varying pyrolysis/gasification conditions.